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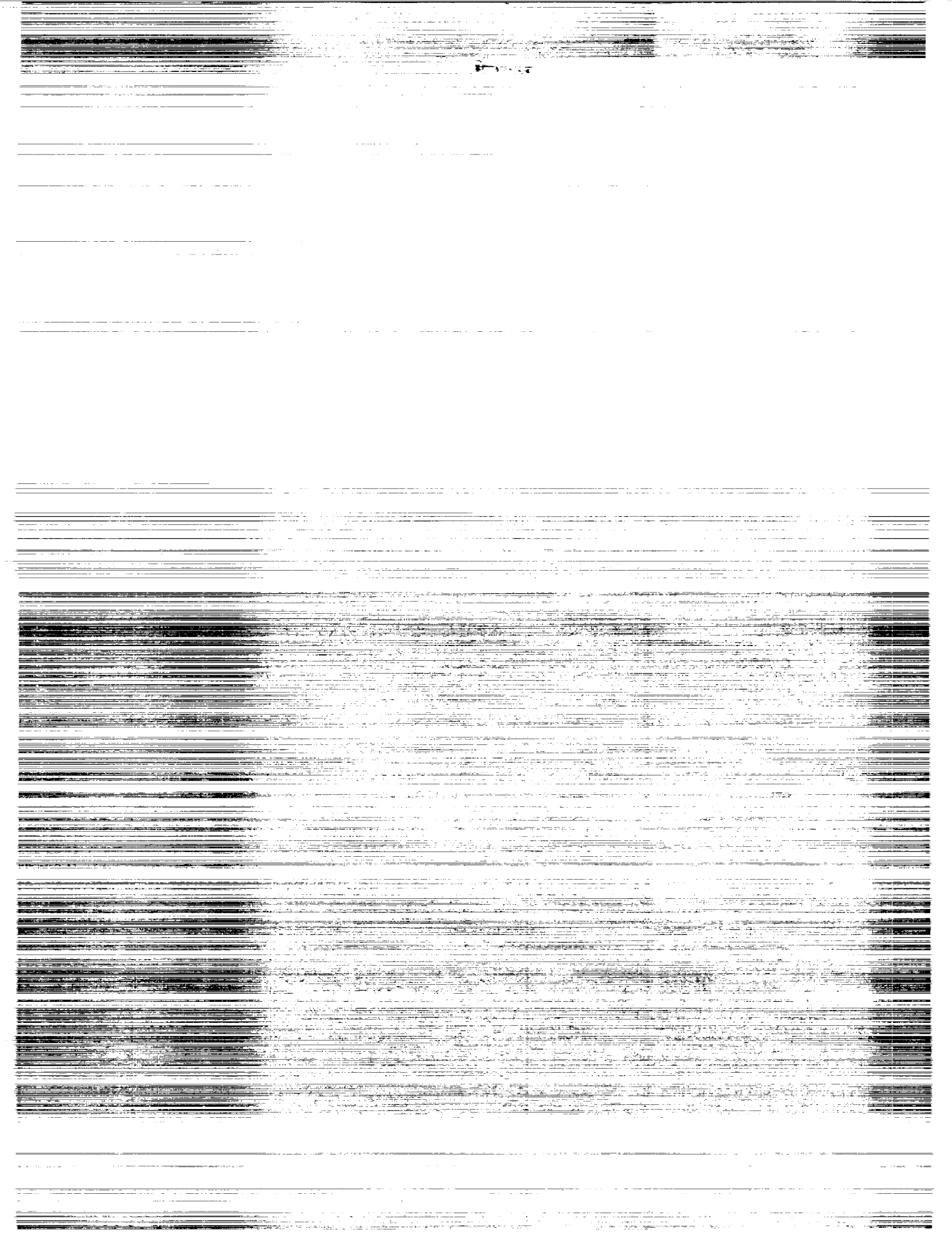

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Low-Energy Positron Flux Generator for Microstructural Characterization of Thin Films

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Summary

A low-energy positron flux generator using well-annealed polycrystalline tungsten moderators and a Na^{22} positron source has been developed for microstructural characterization of thin insulator (ceramics and polymers) films. A 250-μC positron source, deposited on a 2.54-μm-thick aluminized Mylar film, is sandwiched between two 0.0127-cm-thick, 2.54 cm × 2.54 cm tungsten strips. Two 2.54 cm × 2.54 cm test insulator films, whose thicknesses may range from 0.00127 to 0.0127 cm, insulate the two tungsten moderator strips from the aluminized Mylar source holder. A potential difference of 10–100 V, depending on the test insulator film thickness, is applied between the tungsten strips and the source holder. Thermalized positrons diffusing out of the moderator strips are attracted to the source holder when it is at a negative potential. These positrons have to drift through the test insulator films in order to reach the source holder. On the other hand, the positrons are prevented from entering the test films when the source holder is at a positive potential. The difference between the two positron lifetime spectra with the source holder at ±V (volts) is thus expected to provide the test-film lifetime spectrum. Thus, the new generator becomes an effective source of positrons for assaying thin insulator films for their molecular morphology. This report is exclusively devoted to the discussion of applications of the generator to thin polymer (insulator) films.

Introduction

Polymers are finding increasing applications in the aerospace industry. They are strong, lightweight, and can be developed to have desirable mechanical, electrical, and optical properties. Some of the more challenging applications often call for polymers in the form of thin films. The properties of these films are strongly dependent on their molecular morphology. Films with the same chemical composition and density can have different physical properties depending on their processing history. It is therefore necessary to develop a technique that can give information about the internal structure of the "finished" thin polymer films.

We had previously used positron annihilation spectroscopy (PAS) for measuring free volume in polymer discs (refs. 1 and 2). It was therefore decided to adapt conventional PAS to the study of thin films. The *first* attempt involved sandwiching the test films between suitable aluminum degraders such that positrons of progressively higher initial energies were forced to stop in the test films. In order to eliminate the effects of positrons annihilating in the aluminum energy degraders, lifetime spectra were taken *with* and *without* the test films in the target assembly. The difference between these two lifetime spectra represented the test-film lifetime data. However, only a small fraction of the incident positron beam stopped in the test films because of the continuous energy distribution of the Na^{22} positrons. Consequently, it required 24 hours or more to accumulate data with adequate statistics, even with a 50-μC-Na^{22} source.

In order to expedite the data accumulation with better statistics, the following low-energy (slow) positron generation scheme has been devised and implemented: Positrons from a Na^{22} source deposited on a thin, aluminized Du Pont Mylar film are allowed to penetrate a 0.0127-cm-thick, annealed, high-purity (99.95 percent) tungsten strip. After quick thermalization, the incident positrons suffer multiple-scattering collisions with tungsten atoms. A small number of these positrons eventually diffuse back to the surface and are ejected from it with an energy equal to their negative affinity for the tungsten surface (ref. 3). Their energy can be controlled by applying an appropriate electrical potential difference between the tungsten moderators and the aluminized source film. If now a test film is inserted between the moderator and the source, the back-diffusing positrons will enter it when a negative bias is applied to the source holder. These positrons will eventually annihilate in the test film before reaching the source holder. If the potential of the impressed field is reversed, the positrons will be prevented from entering the polymer film. Thus, the difference between the two positron lifetime spectra with ±V (volts) on the source holder gives the spectrum in the test film. The experimental details and some applications of this concept are described in the following sections.

Experimental Design

High-purity (99.95 percent) polycrystalline tungsten pieces in the form of 2.54 cm × 5.08 cm × 0.0127 cm strips were annealed in a 500-μPa vacuum using the following thermal-cycling sequence: Heat the strips to about 1600°C (red hot) by passing a heavy current through them and hold them at that temperature for about 3 minutes; quickly reduce the current to let the strip temperature fall down to about 1000°C; then increase the current to raise the strip temperature back to 1600°C and hold it there for 3 minutes. Repeat the heating/cooling sequence six times before reducing the current to zero to let the strips cool down to ambient temperature while still in the vacuum. The annealed strips were cut into two 2.54 cm × 2.54 cm × 0.0127 cm pieces that served as positron beam moderators. (The moderator strips

require frequent annealing—on the average of twice a week—in order to maintain their conversion efficiency.) A 250-μC Na^{22} source was deposited on a 2.54-μm-thick, 2.54 cm × 5.08 cm aluminized Mylar film. The film was folded into a 2.54 cm × 2.54 cm piece, sealed around open ends, and was inserted between the two moderator strips. The test polymer films, introduced between the source holder and the moderator strips, helped to electrically insulate the source holder from either tungsten strip. The source-moderator assembly is shown in figure 1.

After implantation into the tungsten moderator, the positrons are quickly thermalized. Subsequently, they suffer multiple scattering over distances on the order of 1000 Å before annihilating with the electrons (ref. 4). Some of the surviving positrons diffuse back to the entrance surface from which they are emitted with an energy on the order of $\leq$2 eV. These positrons can be injected into the test sample or pulled back into the moderator by applying the appropriate potential difference between the moderator strips and the source holder. It should be noted that the positrons strike the moderator surfaces almost isotropically, thereby enhancing their probability of eventual escape from the entrance surfaces.

Experimental Procedure

As shown in figure 1, the test polymer films are inserted between the source holder and the moderator strips. Consequently, all reemitted positrons attracted toward the source holder must pass through the test films. They will, in all likelihood, annihilate in the test films before reaching the source holder. Thus, thin polymer films, which could not be conveniently studied for their free-volume characteristics using the multidegrader assembly, can be studied readily by applying a suitable voltage on the source holder.

In order to separate the moderator annihilation spectrum from the test-film spectrum, it is necessary to make two separate lifetime measurements. The *first* measurement is made with the source holder held at a certain negative potential (−V) determined by the sample thickness. In this case, all the positrons diffusing out of the moderator drift into the test film and annihilate in it. The *second* measurement is made with the source holder held at an equal and opposite potential (+V). In this case, the positrons diffusing out of the moderator are pulled back into it.[1] Thus, the number of positrons annihilating in the moderator is larger. In order to correct for this effect, similar lifetime measurements were made in Du Pont Teflon films of comparable thickness. Teflon was selected as the reference material because it has been studied extensively by other authors (refs. 7 and 8) and well-characterized Teflon films and sheets are commercially available. Furthermore, electrostatic field effects in Teflon under the present experimental conditions ($E \approx 3.5$ kV/cm) are negligible (refs. 5 and 6). The fractional excess of positrons remaining in the moderator strips under positive source bias ϵ was then calculated as follows:

$$\epsilon = 2\left[\frac{I_R(-\mathrm{V}) - I_R(+\mathrm{V})}{I_T(-\mathrm{V}) + I_T(+\mathrm{V})}\right] \tag{1}$$

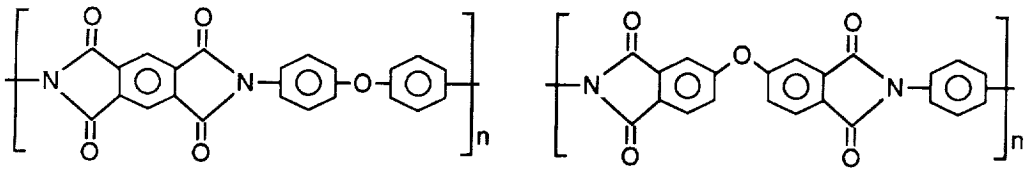
where

$I_R(\pm\mathrm{V})$ total number of counts in the Teflon lifetime spectrum between the time-zero channel and the channel where its lifetime-spectrum intensity decays to the background level

$I_T(\pm\mathrm{V})$ total number of counts in the total (Teflon films plus moderator plus background) lifetime spectrum between the time-zero channel and the channel where the Teflon-plus-moderator lifetime-spectrum intensity decays to the background level

The $I_R(\pm\mathrm{V})$ can be easily separated from the $I_T(\pm\mathrm{V})$ since the Teflon and tungsten lifetime spectra are well-known (refs. 7 and 8). For example, figure 2(a) shows a typical positron lifetime spectrum in a 0.0087-cm-thick Teflon film separating the negatively biased source holder from the grounded tungsten moderator strips. The lifetime spectrum of positrons annihilating in the Teflon films and the moderator strips is clearly visible above the flat background. Similarly, figure 2(b) shows the lifetime spectrum with the source holder at a positive bias with respect to the moderator strips. Both of these spectra are resolvable into three lifetime components τ_1, τ_2, and τ_3 with I_1, I_2, and I_3 as their respective relative intensities. The first two lifetime components (τ_1 and τ_2) correspond to prompt and trapped positron annihilations in tungsten moderators and Teflon films. The third component in both figures is related to orthopositronium decays and, consequently, arises exclusively from positrons annihilating in Teflon since positronium does not form in tungsten moderator strips. Knowing the relative values of intensities for the three lifetime components in thick Teflon discs from the same batch as the test films,

[1]The potential difference across the test film is selected to keep the field across it less than 5 kV/cm in order to minimize/eliminate any field-induced changes in lifetime spectra in it (refs. 5 and 6).



PMDA/ODA ODPA/p-PDA

Sketch A

$I_R(\pm V)$ can be readily separated from $I_T(\pm V)$. It is expected that the relative intensities of the three lifetime components in the Teflon films will be identical with those of the thick Teflon discs from the same batch.

The excess positron fraction ϵ can be considered as the efficiency of the present slow positron flux generator. The excess positron fraction[2] for a 0.0087-cm-thick Teflon film under ± 60 V source bias has been measured to be 4×10^{-2}. It should be emphasized that this fraction simply represents the excess of positrons annihilating inside the test film under negative source bias or, equivalently, inside the moderators under the positive source bias during the Teflon lifetime-spectrum decay interval ($\approx$12 nsec). This fraction should not be confused with the efficiency of the conventional slow positron beam generators (ref. 9) where it represents the ratio of the number of positrons in the slow beam to the total number of positrons emitted from the source. The present system simply produces a low-energy positron flux diffusing out of the moderator strips. These back-diffusing positrons do not constitute a monoenergetic microbeam.

A test-film spectrum is obtained by subtracting the normalized positive source-bias spectrum from the negative source-bias spectrum. This "difference" spectrum is exclusively due to the positrons annihilating in the test films. Figure 2(c) shows the difference spectrum for Teflon films.

Test of the Slow Positron Generator System

In order to test the validity of the assumption that the thermalized positron diffusing back from the moderator surfaces does not suffer inordinate delays (ref. 10) with respect to the 1.28-MeV gamma ray time marker, we compared the lifetimes measured in 0.0087-cm-thin Teflon films using the difference spectrum with the corresponding values in a 0.254-cm-thick disc obtained by using the conventional thick-disc procedure (ref. 11). All measurements were made at room temperature and at atmospheric pressure. The results are summarized in table I. It is apparent that the agreement is reasonably good. Thus, the present system successfully resolves the difficult timing problem often encountered with the microbeam positron generators (ref. 10). Furthermore, the system operates at room temperature and atmospheric pressure with no special test-film preparation requirements.

Applications

We have used the slow positron generator system for the measurement of free-volume fraction in two types of polyimide films. The physical properties (ref. 12) of these films are summarized in table II. The polyimide PMDA/ODA was prepared by the NASA Langley Research Center and has the same chemical structure as Du Pont Kapton (Du Pont's commercially available polyimide). The polyimide ODPA/p-PDA is an isomer of PMDA/ODA. Sketch A shows the chemical structure of the two isomers. The PMDA/ODA is essentially a totally amorphous polymer, whereas the ODPA/p-PDA has a significant level of crystallinity. This crystallinity results in a high modulus in the latter polymer (6.722 GPa) as compared with 2.62 GPa in PMDA/ODA. Even though the two systems are isomers of each other, they obviously have considerable differences in their morphologies.

Positron lifetimes in these two types of films were measured using the standard fast-fast coincidence lifetime measurement technique based on the present slow positron flux generator. Each spectrum required about 2×10^4 sec of data acquisition time to obtain good statistics. These spectra were analyzed using the POSFIT-EXTENDED program (ref. 13). The free-volume fractions in these films were then calculated using the relationship (refs. 14 and 15)

[2]In the absence of any source bias, only those positrons in the incident beam whose range in the test film is equal to or less than the test-film thickness will stop in it. They constitute only a small fraction ($\approx 10^{-5}$) of the total beam.

between the orthopositronium lifetime and the average microvoid size in the polymers. Figure 3(a) shows a comparison between the lifetime spectra observed in 0.0087-cm-thick PMDA/ODA films with the source bias at ±60 V. Clearly a smaller fraction of positrons annihilate in the test films when the source bias is positive. Figure 3(b) shows a comparison between −60 V and the zero source-bias spectra. Here again, fewer positrons annihilate in the test films when there is no bias on the source holder. Figure 3(c) shows a comparison between +60 V and the zero source-bias spectra. In this case, on the other hand, the number of positrons annihilating in the test films is approximately the same. Clearly, the back-diffusing positrons fail to enter the test films without a guiding field. Figure 3(d) shows the difference spectrum obtained by subtracting the normalized positive bias spectrum from the negative bias spectrum. This spectrum represents the true lifetime spectrum in the PMDA/ODA films.

The positron lifetimes and the corresponding values of the average free-volume cells $< V_f >$ in the test films are summarized in table III. The free-volume sizes have been calculated (refs. 14 and 15) assuming that lifetimes in excess of 500 psec can be attributed to orthopositronium in these materials. Clearly, ODPA/p-PDA films have larger microvoids, although there are comparatively fewer of them.

Concluding Remarks

A low-energy positron flux generator suitable for positron annihilation spectroscopic (PAS) measurements in thin polymer films has been developed. Its efficiency, determined by the ratio of the difference in the counts in the Teflon film lifetime spectra with the source biased at ±V (volts) and the average of the total lifetime spectra counts within the Teflon spectrum decay period, has been calculated to be 4×10^{-2}. The present scheme also successfully resolves the difficult timing problem often encountered in the positron microbeam generators. Its critical advantage over conventional low-energy positron beam generators is its ability to operate at room temperature and at atmospheric pressure with no special test-film preparation requirements.

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March 22, 1991

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Table I. Comparison Between Positron Lifetimes in Teflon Measured With Present System and Conventional System

[τ denotes lifetime component; I denotes corresponding relative intensity]

(a) Present system[a]

Positron lifetime values with—		
τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3, psec/percent
279 ± 4/56 ± 1	781 ± 10/27 ± 1	3980 ± 37/17 ± 1

[a]Source = 250 μC; Source holder bias = ±60 V; Teflon target thickness = 0.0087 cm.

(b) Conventional system[b]

Positron lifetime values with—		
τ_1/I_1, psec/percent	τ_2/I_2, psec/percent	τ_3/I_3, psec/percent
269 ± 3/56 ± 1	809 ± 16/26 ± 1	3911 ± 37/18 ± 1

[b]Source = 25 μC; Teflon target thickness = 0.254 cm.

Table II. Physical Properties of Test Polyimide Films

[Data taken from ref. 12]

Film type	Film thickness, cm	Coefficient of thermal expansion, μm/m-°C	Density, g/cm^3	Tensile modulus at 25°C, GPa	Saturation moisture, volume percent (v/o)
PMDA/ODA	0.0087	23.3	1.414 ± 0.003	2.620×10^9	4.46
ODPA/p-PDA	.0100	23.8	≥1.45	6.722×10^9	2.61

Table III. Summary of Free-Volume Results in Test Polymer Films

[Source = 250 μC Na^{22}; bias = ±60 V]

Film type	Positron lifetime values		$<V_f>$, Å^3	N^a
	τ_1/I_1, psec/percent	τ_2/I_2, psec/percent		
PMDA/ODA	273 ± 2/71 ± 1	550 ± 41/29 ± 1	0.71	6.2×10^{22}
ODPA/p-PDA	246 ± 6/79 ± 4	837 ± 16/21 ± 4	10.40	2.6×10^{21}

[a] N denotes the number of free-volume cells per cubic centimeter:

$$N = \frac{\text{Saturation moisture volume/cm}^3}{<V_f>} = \frac{\text{Total fractional free volume/cm}^3}{\text{Average volume of free-volume cell (cm}^3\text{)}}$$

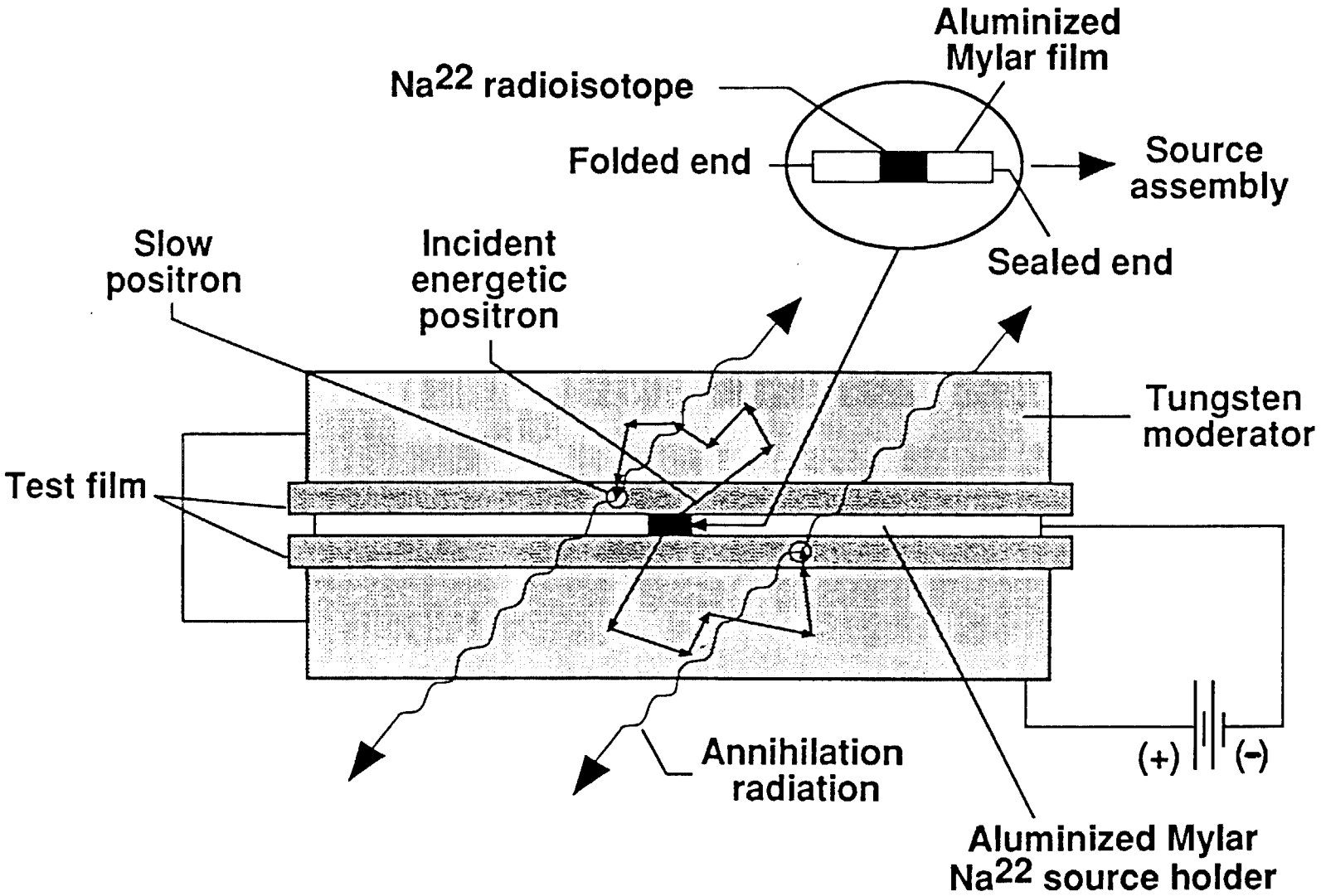
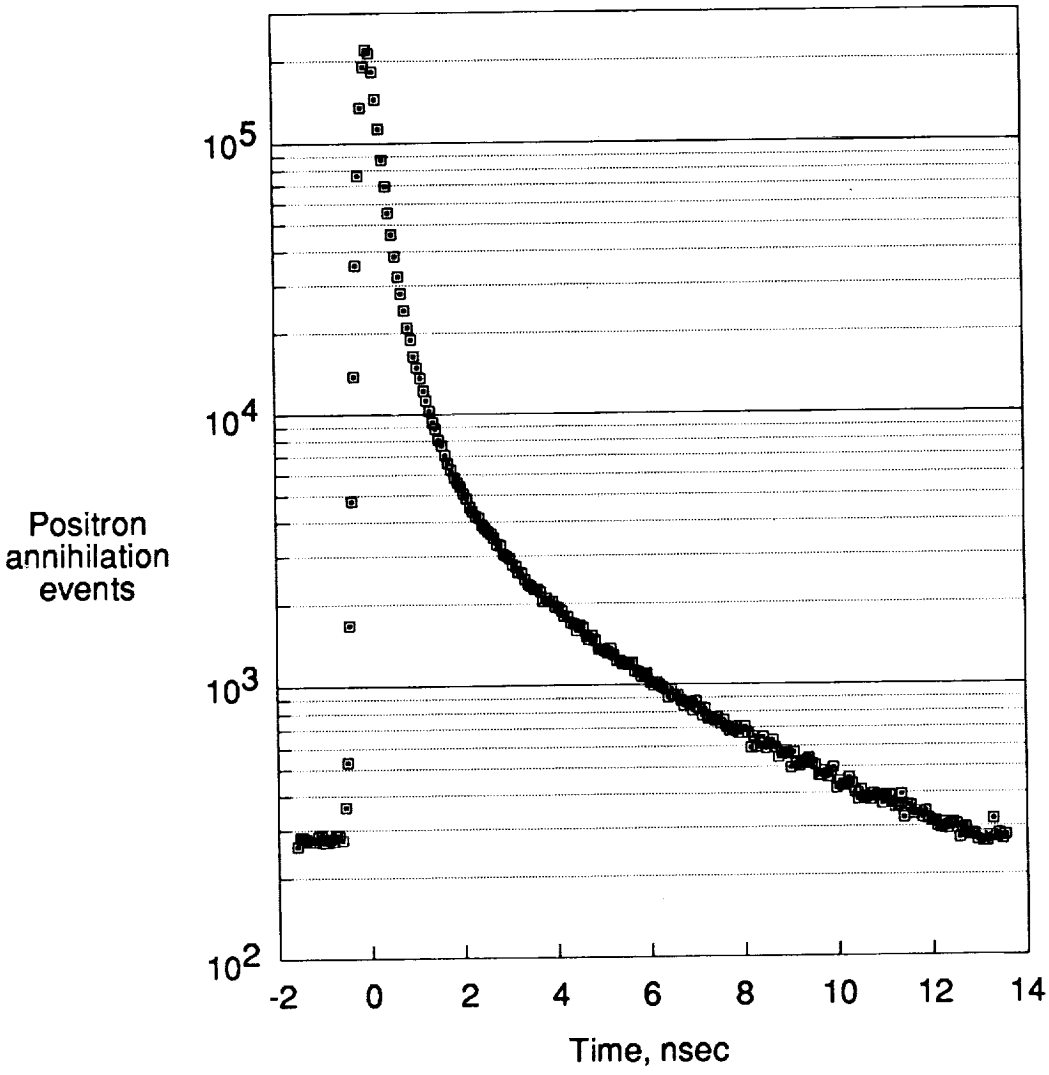
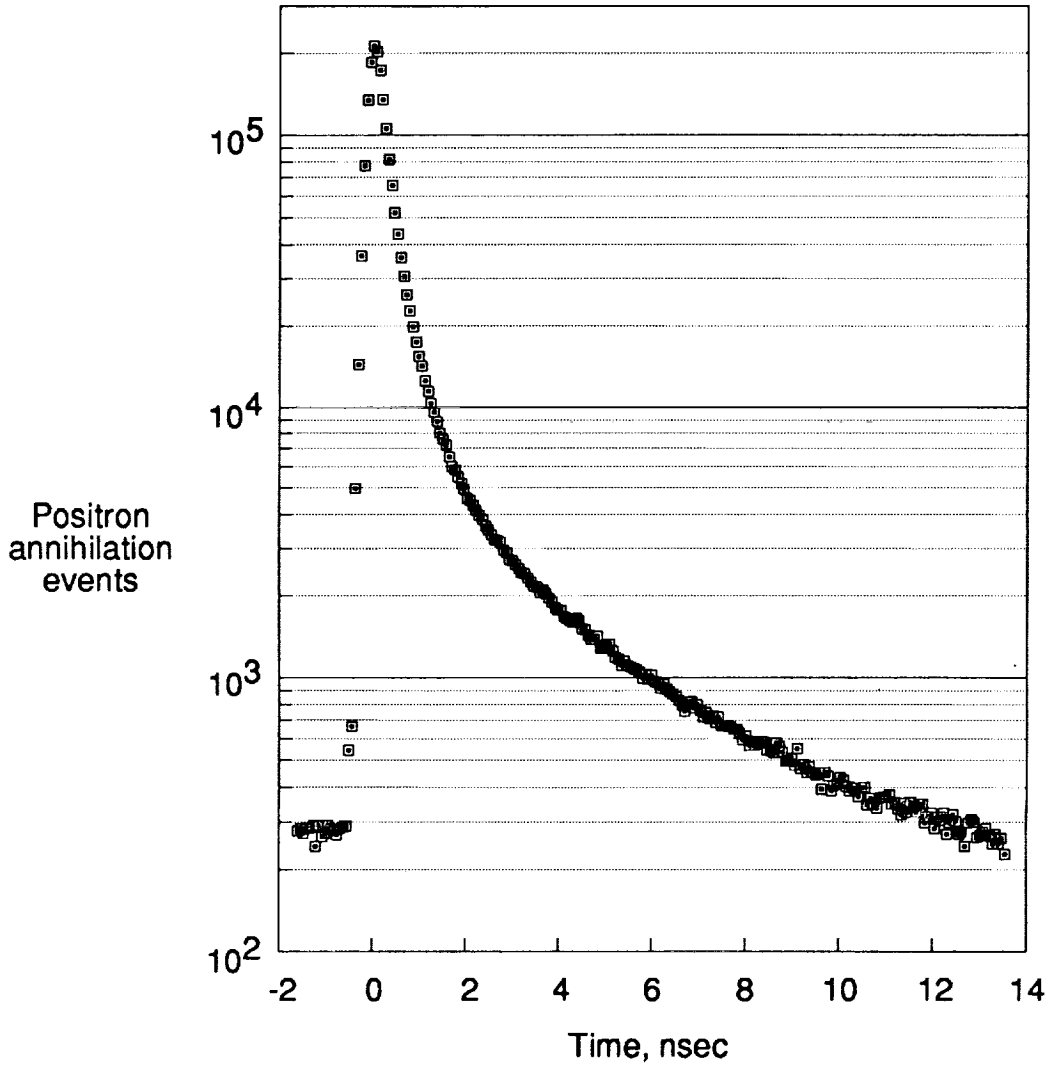


Figure 1. Schematic diagram of source-moderator assembly.



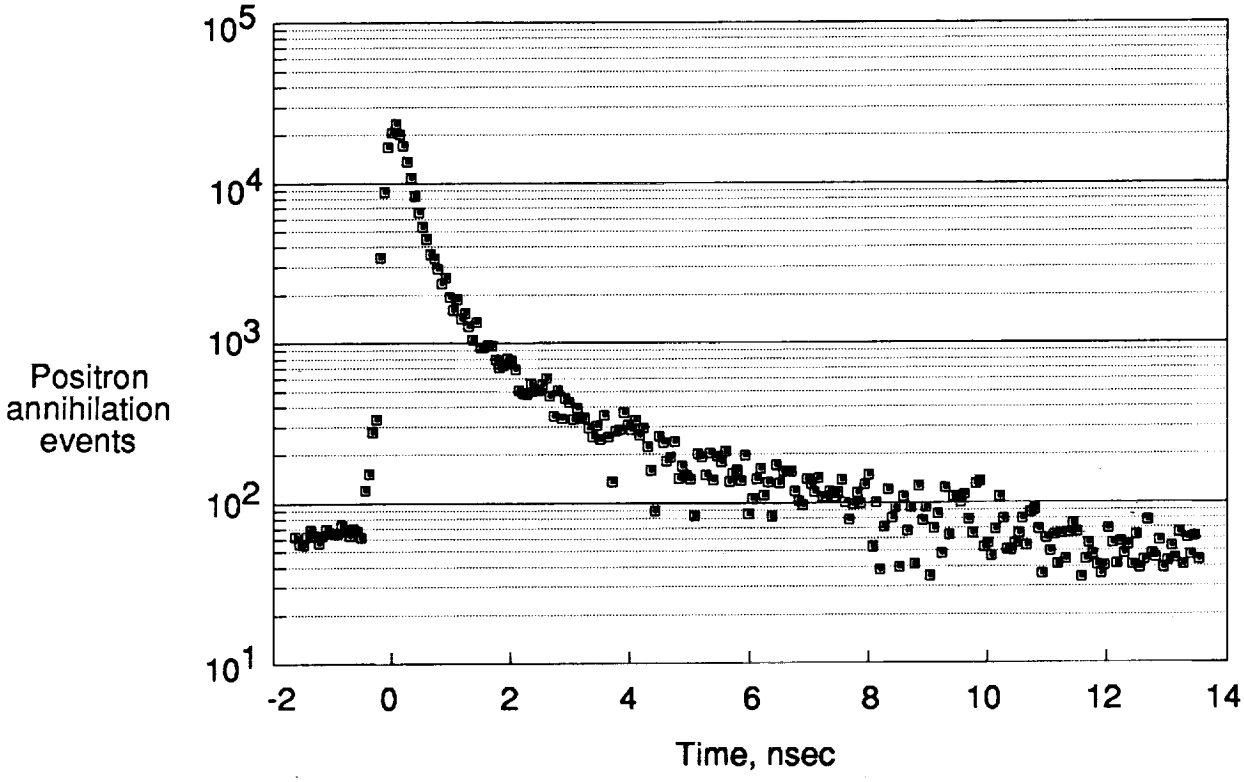
(a) Source holder at −60 V.

Figure 2. Teflon film spectrum.



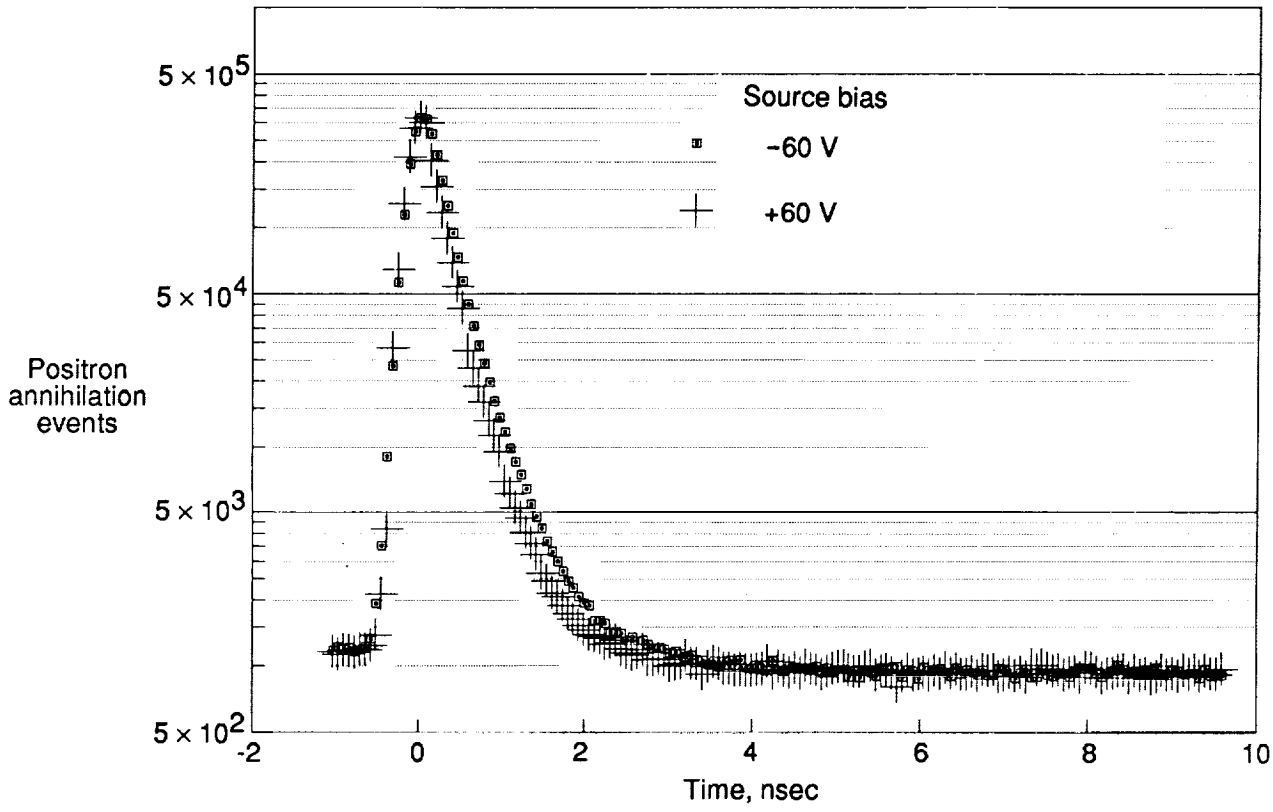
(b) Source holder at +60 V.

Figure 2. Continued.



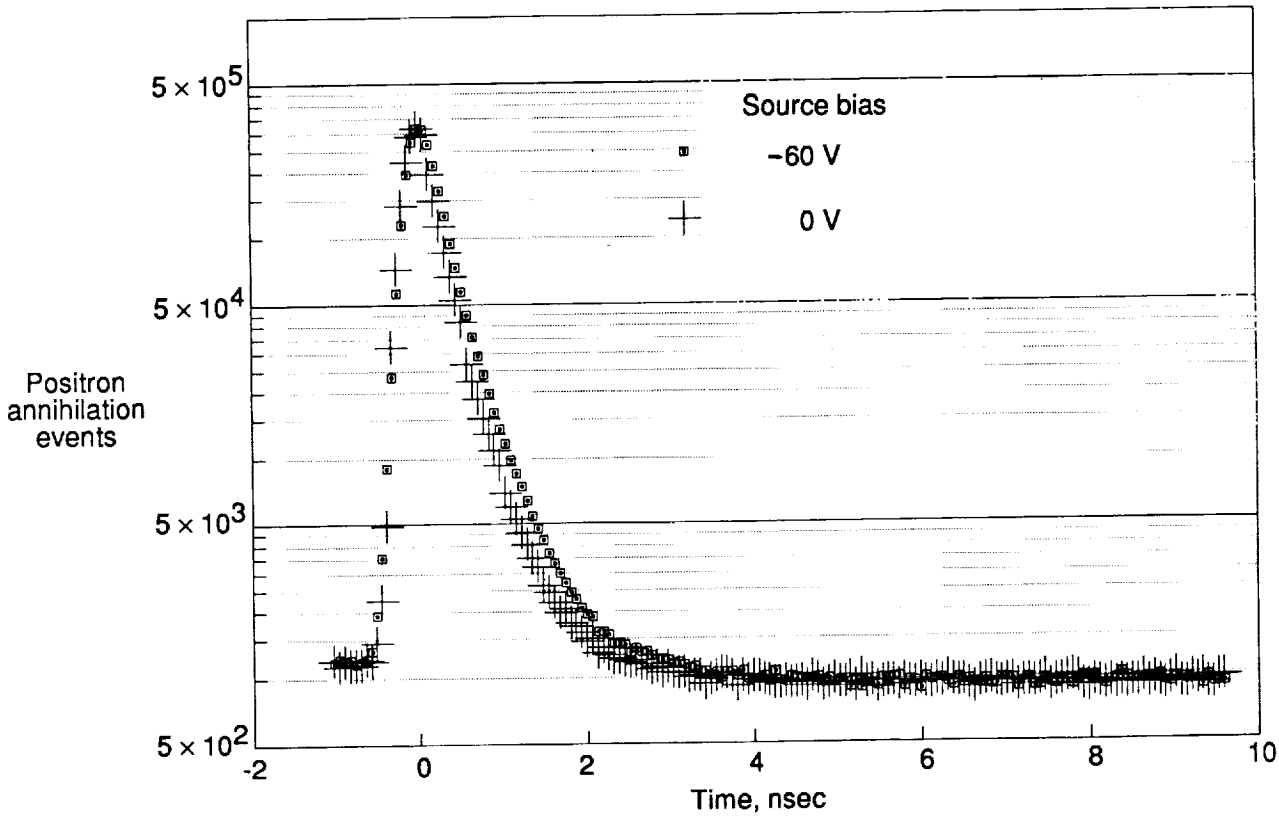
(c) Positron lifetime spectrum in Teflon film obtained by subtracting normalized positive bias spectrum from negative bias spectrum.

Figure 2. Concluded.



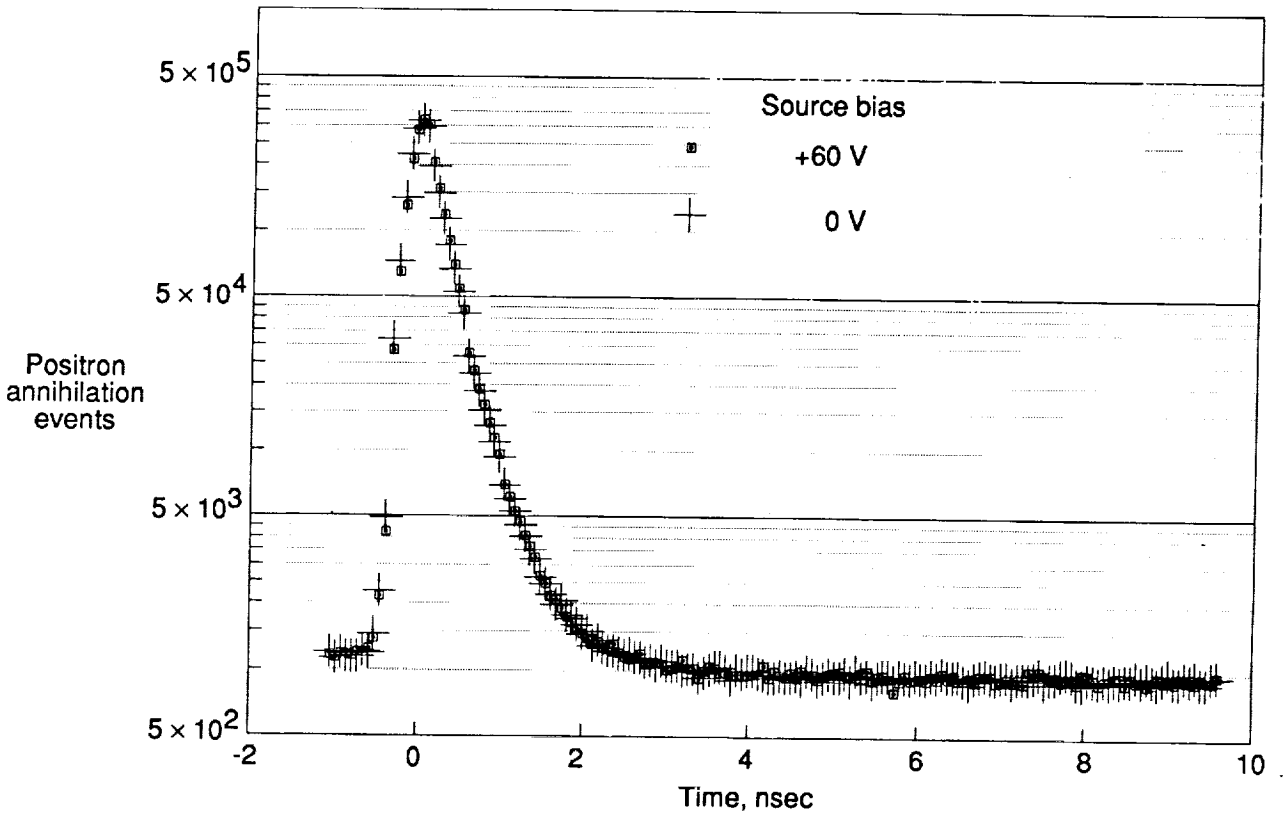
(a) Comparison between positive and negative source-bias lifetime spectra in PMDA/ODA films.

Figure 3. Lifetime spectra in PMDA/ODA films.



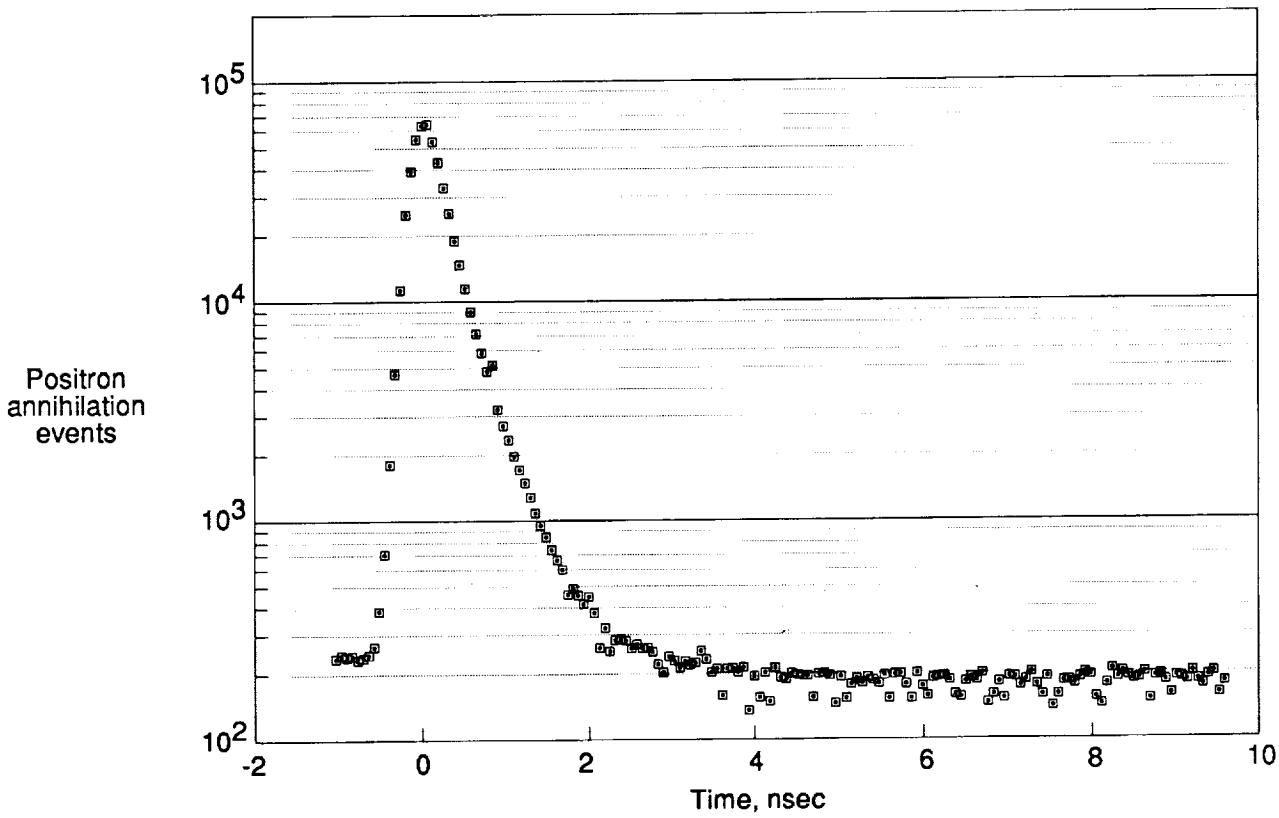
(b) Comparison between negative and zero source-bias lifetime spectra in PMDA/ODA films.

Figure 3. Continued.



(c) Comparison between positive and zero source-bias lifetime spectra in PMDA/ODA films.

Figure 3. Continued.



(d) Positron lifetime spectra in PMDA/ODA films obtained by subtracting normalized positive bias spectrum from negative bias spectrum.

Figure 3. Concluded.

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16. Abstract

A low-energy positron flux generator using well-annealed polycrystalline tungsten moderators and a Na^{22} positron source has been developed for microstructural characterization of thin insulator (ceramics and polymers) films. A 250-μC positron source, deposited on a 2.54-μm-thick aluminized Mylar film, is sandwiched between two 0.0127-cm-thick, 2.54 cm $\times$ 2.54 cm tungsten strips. Two 2.54 cm $\times$ 2.54 cm test insulator films, whose thicknesses may range from 0.00127 to 0.0127 cm, insulate the two tungsten moderator strips from the aluminized Mylar source holder. A potential difference of 10–100 V, depending on the test insulator film thickness, is applied between the tungsten strips and the source holder. Thermalized positrons diffusing out of the moderator strips are attracted to the source holder when it is at a negative potential. These positrons have to drift through the test insulator films in order to reach the source holder. On the other hand, they are prevented from entering the test films when the source holder is at a positive potential. The difference between the two positron lifetime spectra with source holder at $\pm$V (volts) is thus expected to provide the test-film lifetime spectrum.

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